

A Current Induced Transition in atomic-sized contacts of metallic alloys

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We have measured conductance histograms of atomic point contacts made from the noble-transition metal alloys CuNi, AgPd, and AuPt for a concentration ratio of 1:1. For all alloys these histograms at low bias voltage (below 300 mV) resemble those of the noble metals whereas at high bias (above 300 mV) they resemble those of the transition metals. We interpret this effect as a change in the composition of the point contact with bias voltage. We discuss possible explanations in terms of electromigration and differential diffusion induced by current heating.

I. INTRODUCTION

The scale of electronic devices will soon be reduced to a level where material properties will be very different from the bulk, necessitating research into very small scale devices. A metallic point contact is perhaps the most simple example of an atomic-sized device. It consists of a connection of a few atoms, typically between 1 and 1000, between two macroscopic electrodes. The size of the contact is therefore of the same order of magnitude as the Fermi wavelength of the electrons. In this limit, the conductance is related to the transmission of an electron wave through the system. For a free electron gas, the transmission only depends on the size of the constriction. As a result, the conductance in a 2-dimensional electron gas has been seen to increase by steps as a function of the width of the constriction^{1,2}. The situation is more complicated in a metallic contact, where the transmission depends on the geometry of the contact as well as on the atomic structure of the atoms forming it. In the simplest case the contact consists of a single atom, where the conductance has been shown to be determined by the valence orbitals of the atom forming the contact^{3,4}.

Several ways exist to create a point contact. The method used in this research is the so-called mechanically controllable break junction (MCBJ) technique⁵. Its principle is very simple; it consists of breaking a metallic wire thereby creating a clean fracture surface. After rupture, an atomic-sized contact can be made by indenting the broken ends of the wire into each other. This contact is subjected to a repeated cycle of breaking and indenting, during which the conductance of the contact is measured. As the contact is elongated, the diameter of the constriction reduces and consequently the conductance decreases.

For most metals at small contacts, the conductance decreases in steps of the order of $G_0 = 2e^2/h$, the quantum of conductance. It has been shown that these steps are due to rearrangements of atoms in the contact⁶. The

last plateau is generally assumed to correspond to a single atom contact⁷.

The electrical and mechanical properties of atomic point contacts made from pure metals have been extensively studied^{8–11}. For noble metals (Cu, Ag, Au) the last plateau of a conductance trace, corresponding to a contact of one atom, has a conductance value around $1 G_0$. On the other hand, transition metals (of which we will consider Ni, Pd, Pt) have a smallest conductance value around $1.5 G_0$, or higher. These values are explained by the fact that noble metal atoms have a single s valence orbital and transition metal atoms have five d valence orbitals in addition. Very few studies have been made of the properties of *alloys* at the atomic scale.

Recently, point contact studies were made of random alloys of a transition metal and a noble metal, namely gold and palladium¹² and copper and nickel¹³, for different concentration ratios. For AuPd, the addition of Pd only leads to a decrease in height of the Au conductance peak, and no shift is observed. We propose below a different explanation for the persistence of the Au peak up to a high concentration of Pt or Pd. The CuNi study was aimed at an investigation of the influence of impurity scatterers on the point contact conductance. For low Ni concentrations the nickel atoms can be considered as impurity scatterers for the electrons, that lead to a decrease of the conductance resulting in a shift towards lower values of the peaks in the conductance histogram. This shift grows linearly with the Ni concentration. For higher concentrations of transition metal atoms, it is difficult to predict how the contact will behave and what effects might occur. Naively, one would expect a single-atom contact to be randomly formed by either a noble (Cu, Au) or a transition metal (Ni, Pd) atom, with a probability depending on concentration. However, this does not take into account several effects that could influence the formation of the contact, such as segregation, diffusion and possibly electromigration. Indeed, here we show that this simple picture does not hold. In addition

we report an unexpected transition in the conductance characteristics as a function of the bias voltage for random transition-noble metal alloys. Complementary to the experiments we have performed molecular dynamics simulations in order to obtain information on the structure and composition of the atomic point contacts that is not provided by a conductance measurement.

II. EXPERIMENT

The alloys that were used in this experiment, apart from copper-nickel, were silver-paladium and gold-platinum, all at a 1:1 concentration ratio. These materials were chosen for the following reasons: First, they are miscible at any concentration. Second, the conductance of the noble metal atoms (Cu, Ag, Au) is different from that of the transition metal atoms (Ni, Pd, Pt), (see above) which allows us, in principle, to distinguish single-atom contacts of noble metals and those of transition metal atoms.

Samples were made by arc-melting equal amounts of Cu (Ag, Au) and Ni (Pd, Pt) and quenching to room temperature. CuNi and AgPd form random alloys. Below ~ 1260 C, AuPt may segregate, but we see little evidence for segregation in our data. Of these samples wires are made and annealed for several hours at 900 C. A 1.5 cm long piece of wire is then glued on a phosphor-bronze substrate by two drops of epoxy on both sides of a notch made in the middle of the wire. The wire is broken at low temperature (4.2 K) by applying a mechanical force on the substrate. The two broken ends are then brought back together and the bending is controlled by means of a piezo element allowing us to obtain a contact of any size, where the contact elongation can be controlled with an accuracy better than 0.01 \AA . The conductance is measured in a four point configuration.

Individual conductance traces (plots of the conductance vs the elongation of the wire) differ from each other because the positions of the atoms are different each time a new contact is formed. For a more quantitative view of the conductance of the contact a histogram technique is used that will indicate preferred values of the conductance when the size of the contact decreases. A histogram is constructed as follows: the y -axis of an individual conductance trace is divided into a number of bins and we count the number of data-points that fall in those bins. Peaks in the histogram represent preferred values of the conductance.

Histograms were created from ~ 2500 individual conductance traces. Between these individual traces the broken ends of the wire are indented to a large contact size that is set by a predetermined value for the conductance. The usual indentation depth was to a conductance of $25\text{--}30 G_0$, corresponding to a contact of approximately as many atoms.

For a further investigation of the noble-transition

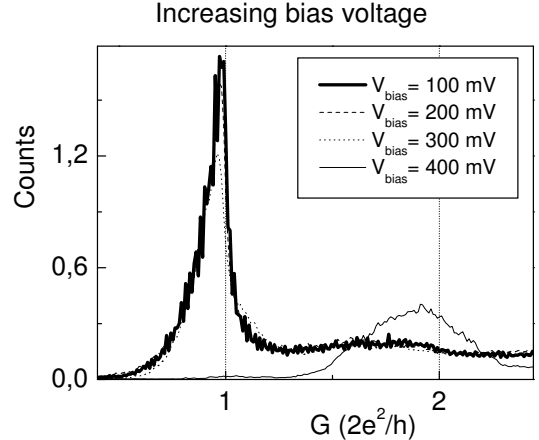


FIG. 1. Normalized histogram for AuPt for different bias voltages, starting from 100 mV and increasing to 400 mV. The position of the peak changes from $0.95 G_0$ to $1.9 G_0$ when the bias voltage is increased from 300 to 400 mV. The indentation of the contact after each scan was to a conductance of $30 G_0$.

metal point contacts, classical molecular dynamics simulations have been performed on a CuNi point contact. The system was simulated using two-atom potentials and a Johnson-Oh embedding function formalism¹⁴. The motion of the atoms in a point contact of a random alloy at low temperature was calculated while the contact was being stretched.

III. RESULTS

In Fig. 1 histograms of AuPt recorded with four different voltages applied across the contact (bias voltage) are shown. All histograms are normalized by the area under the curves in the interval $[0, 10] G_0$. The histogram at low bias voltage exhibits a strong peak positioned somewhat below $1 G_0$. The amplitude of the peak initially decreases slightly as the bias voltage is increased but at $V_{\text{bias}} = 400$ mV it has disappeared and instead a peak positioned at $G \simeq 1.9 G_0$ appears. It is important to notice that this peak is located approximately at the position of the first peak of pure Pt.

Measurements of the conductance of copper-nickel and silver-paladium showed that also for these alloys the low bias voltage histogram resembles that of the noble metal having a dominant peak slightly below $1 G_0$, while at high bias it resembles the conductance histogram of the transition metal and all the weight below $1.5 G_0$ has disappeared.

After a high bias voltage measurement, decreasing the voltage across the contact did not result in a return to a noble-metal-like histogram, as can be seen in Fig. 2. For all alloys, only after full indentation of both ends of the wire (by putting the voltage on the piezo to zero),

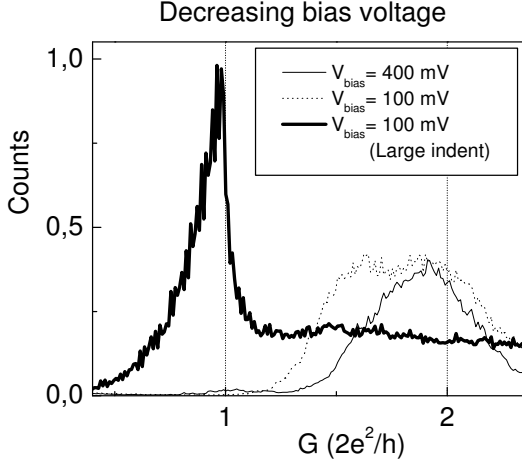


FIG. 2. Histogram of AuPt when decreasing the bias voltage for different values above and below the critical value for inducing the transition. The peak around $1 G_0$ does not reappear unless a large contact is made. The indentation of the contact after each scan is to a conductance of $30 G_0$.

creating a contact of mesoscopic size (> 1000 atoms), a noble-metal-like histogram was recovered.

From a conductance histogram it is impossible to tell whether the shift in conductance is gradual or sudden since the histogram is accumulated from many conductance scans. Therefore we decided to measure a number of subsequent histograms of a smaller number of scans (500–1000) to be able to observe possible time-evolution of the contact. Again, the results are similar for the three alloys. At intermediate bias voltage (between 300 and 400 mV) it is possible to observe the change from a noble to transition-metal-like conductance histogram over the course of a small number of histograms as can be seen in Fig. 3.

We have also studied the influence of the indentation depth of the broken ends of the wires on the transition in the contact. In this experiment, the largest contact size between individual traces of a histogram was varied for a number of histograms. This contact size between traces is a measure for the indentation depth, and is characterized by a certain conductance value. It is observed (Fig. 4) that at smaller indentation depth the change from noble to transition-metal-like appears sooner (both at lower bias voltage and in a shorter time period) than for larger indentation. The additional fine structure in the case of very small indentation ($10 G_0$) in Fig. 4 can be explained by the fact that at small indentation the number of possible atomic configurations is reduced compared to a large indentation, and consequently the number of conductance values is limited. At very low indentation depths this can result in a repetition of a limited number of evolution paths for the contact.

In order to determine if the transition is related to the direction of the current in the contact we have conducted

the same experiment using an ac voltage instead of a dc one. The frequency of the bias voltage was $\omega = 10$ kHz, which was limited by the frequency transfer characteristics of our setup. The current and voltage over the sample were detected using two lock-in amplifiers. We found that the results obtained from the ac-voltage experiment are similar to ones from the dc-experiments. We conclude that the transition is not related to the direction of the current, at least for time scales longer than 0.1 ms.

In the molecular dynamics simulations, a random alloy of copper and nickel atoms was created, shaped like an hourglass, which was subjected to about 30 cycles of indenting and breaking of the contact at a temperature of 4K. The main outcome of the simulations is that the randomness of the alloy is preserved; no segregation was observed for up to 18 cycles of indentation to a contact size of 10–50 atoms and subsequent breaking. Our model does not allow us to simulate an electrical potential across the contact or a current through it. Another significant drawback is the fact that even though the timescale of the simulation was $\sim 10^{-9}$ s, which is 8 orders of magnitude smaller than in the experiment, the calculation time was one or two days for a single cycle, thus limiting the number of simulations we could perform.

IV. DISCUSSION

As is illustrated for Au and Pt in Fig. 5, at low bias voltage the histograms of the alloys resemble the histograms of the noble metals (Cu, Ag, Au) rather than those of the transition metals (Ni, Pd, Pt), with a distinct peak slightly below $1 G_0$, but no peak around ~ 1.5 – $1.8 G_0$. However, when a high bias voltage is applied

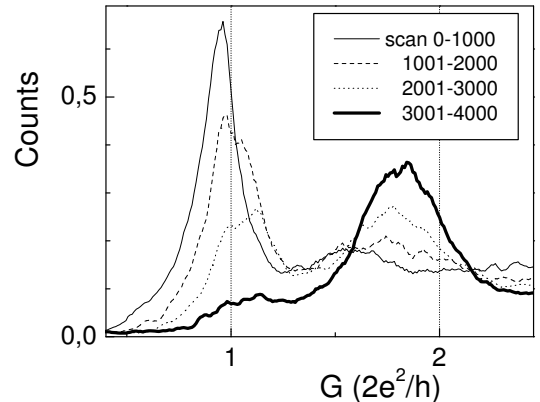


FIG. 3. Time dependence of the conductance of an AuPt point contact, starting from a low-bias structure. One can observe the gradual change in the conductance peak from ~ 0.95 to $\sim 1.8 G_0$. The bias voltage is 375 mV, the indentation of the contact after each scan is to a conductance of $30 G_0$. The time elapsed between scan 1 and scan 4000 is approximately 1500 s.

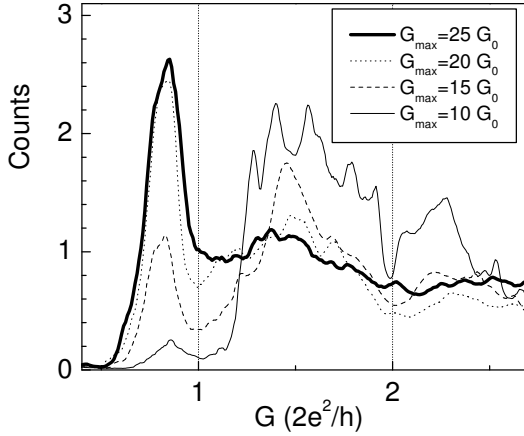


FIG. 4. Histogram for a AgPd point contact for different indentation depths at $V_{\text{bias}} = 220$ mV. For each histogram we start from a contact having a fresh low-bias characteristic structure. One can observe that the transition occurs faster at smaller indentation.

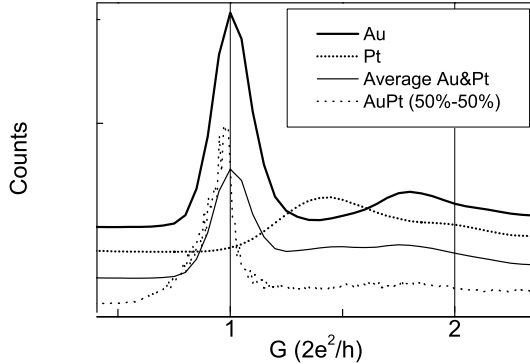


FIG. 5. Histograms of pure gold, pure platinum, their average and a histogram of gold-platinum measured at low bias voltage. The graphs are shifted on the y-axis for clarity.

to the contact the picture is reversed. In fact, for bias voltages above the threshold value the conductance histogram only exhibits a peak located at a conductance value of $1.5\text{--}1.8 G_0$, and is therefore similar to a transition metal histogram.

This suggests that as a result of the bias voltage applied across the contact the noble metal atoms are expelled from it, and only transition metal atoms remain. The peak around $1 G_0$ for low-bias voltage indicates the presence of noble metal atoms; the fact that there is no weight in the conductance histogram below $1.5 G_0$ in case of a high-bias voltage indicates the absence of noble metal atoms.

From the time dependence of the current-induced changes we conclude that the composition of the contact is irreversibly modified, locally. Fig. 3 illustrates how this modification gradually builds up and Fig. 2 shows that the initial properties are only recovered after making a

large indentation. These observations can be understood by assuming that Au (Cu, Ag) atoms are driven away from the contact at high bias, leaving a nearly pure Pt (Ni, Pd) contact. After indentation to large contacts fresh Au (Cu, Ag) atoms are anew mixed into the contact area. The importance of the irreversibility of the shift with bias voltage should not be underestimated. It indicates that the shift cannot be attributed to a straightforward effect in pure metals, since such an effect would be reversible.

This view is supported by the fact that the transition is also dependent on the indentation depth. At higher indentation depths the transition takes place at a higher bias voltage. This agrees with the larger region that has to be depleted of noble metal atoms for larger indentation depths in order to have a contact consisting purely of transition metal atoms. The number of atoms which have to be expelled therefore increases with the indentation.

There are two principle candidates for explaining the observed change in composition of the contacts when a bias voltage is applied across the contact: electromigration, and differential thermal diffusion. Electromigration is the motion of atoms in a conductor under the influence of an applied voltage. It is traditionally described in terms of a direct force and wind force^{15,16}. The direct force is believed to be due to the electric field and the effective charge of the atom, and the wind force is due to the scattering of the current carrying electrons resulting in a momentum transfer. More recent work suggests that it is not meaningful to distinguish these two components and that one should consider the total force to be due to an induced bias in activation barriers for migration¹⁷.

Scattering of current-carrying electrons causes Joule heating of the contact^{18–20} resulting in a temperature gradient leading to a diffusion of atoms away from the contact. This could lead to a change in the composition of the contact when the diffusion coefficients of the different types of atom are unequal. The type of atom with the largest diffusion coefficient would be expelled from the contact. We estimate that a bias voltage of 400 mV raises the lattice temperature locally to ~ 400 K^{18–20}. The diffusion constants for the noble metals are usually much larger than those for the transition metals.

The experiments discussed above all support the view that the composition of the contact is changed, but unfortunately they do not shed any light on the mechanism behind it. The dependence of electromigration on the direction of the current could possibly allow us to distinguish between thermal diffusion and electromigration. In an ac-experiment the direction of the electrical force would change with the potential. When the polarity of the potential changes rapidly the average force on the atoms would be negligible, and only thermal diffusion would remain as a possible cause for the transition. The result of the ac-experiments were the same as those from the dc-experiments. Therefore we conclude that the transition in the contact is more likely due to the second effect. Electromigration is not fully excluded

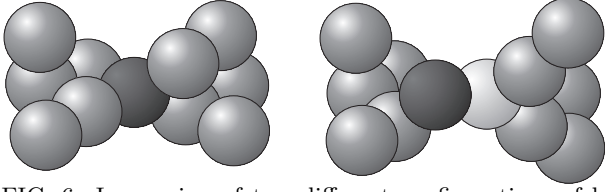


FIG. 6. Impression of two different configurations of last contact, formed by one atom (dark, left) or two atoms in series (dark and light, right).

since the gradient in the current density would drive the atoms away from the contact area, making the return path much less effective.

The outcome of the simulations did not show a preference for the formation of noble-metal last atom contacts over transition-metal atom contacts. The fact that we could not simulate a voltage or current in the contact prevents us from investigating a possible preference for the formation of transition metal atom contacts at high bias. However, the simulations did shed some more light on the dynamics of the point contact. In the discussion we have previously assumed that the last contact would be formed by one atom between the two shoulders of the banks. In the simulations we observed that the last contact is often formed by two atoms, one in each shoulder, see Fig.6.

This changes the question of what the conductance of a noble- or transition-metal-atom contact is, to the question of what is the conductance of a contact between a noble and a transition-metal atom. Based on the work in Refs.^{3,4} we speculate that the conductance of a contact between a copper and a nickel atom is determined by the copper atom, since it has the smallest number of valence orbitals or conductance channels, which would limit the conductance to a single channel with a conductance somewhat below $1 G_0$. If, as the simulations suggest, most of the final contacts are formed by two atoms in series, then $\sim 75\%$ of the final contacts would have approximately the conductance of copper. This may also explain why we cannot distinguish a nickel conductance peak in the CuNi low bias histogram, since one would expect only $\sim 25\%$ of the contacts to be formed by two nickel atoms. Thus, the conductance histogram of CuNi would resemble the copper histogram with a peak below $1 G_0$. The assumption that the conductance between two atoms is determined by the atom with the smallest number of conductance channels remains to be further investigated. However, recent work on a hydrogen molecule trapped between two Pt electrodes shows that this system has a single nearly fully transmitting conductance channel, presumably due to the single s orbital of hydrogen²¹.

In conclusion, we have investigated atomic point contacts made from the noble-transition metal alloys AuPt, CuNi, and AgPd at a concentration ratio of 1:1. At low bias voltage the histograms resemble the ones of the no-

ble metals whereas this situation is reversed at high bias. Our interpretation is that the contact is depleted of noble metal atoms with high bias. The concentration can therefore be tuned with the bias voltage. The mechanism we propose relies on the strong local gradients in lattice temperature and/or current density, driving the noble-metal atoms away from the junction at high voltage bias.

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